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Research under this contract covered theoretical studies of atom-molecule reactive collisions and of electron-molecule scattering. In both cases the principal emphasis was on development of theoretical methods designed for computational studies useful in interpreting or refining experimental results.

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THEORY OF ELECTRONIC, ATOMIC, AND MOLECULAR COLLISIONS

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I. INTRODUCTION AND BACKGROUND

This document is the final report on Contract N00014-79-C-0406, for the period June 1979 through July 1983. Part of the work is continuous with that supported under Contract N00014-72-C-0051, which terminated in March 1978 and under Contract N00014-78-C-0447, which terminated in May 1979.

Research under this contract has been concerned with the theoretical study of atom-molecule reactive collisions and of electron-molecule scattering. In both areas, the principal emphasis has been on the development of theoretical methods that are designed for computational studies useful in interpreting or refining experimental results.

Principal published results of work supported by this contract over its four-year period are summarized in Section II. Work done in the most recent contract period, June 1982 through July 1983, is described in Section III. Results have been reported in thirty-one publications listed in Section IV.

II. PRINCIPAL RESULTS

A. Studies of Surprisal Theory

Information theory has been used with considerable success to analyze molecular collision processes.[1] In many cases, final state population distributions of atom-molecule collision products are closely approximated by a linear surprisal law. This implies that the information content of the population distribution is minimal, subject to a single dynamical constraint condition

To examine the relationship of such results to the underlying collision dynamics, a formalism was devised in which it is possible to study the evolution of internal state populations as a function of a collision coordinate in a reactive collision. Dynamical entropy is defined as a statistical property of a dynamical scattering matrix, indexed by internal states of a molecular collision system for a specified value of a reaction coordinate. Earlier studies of coplanar $H+H_2$ with this formalism were extended to the three-dimensional $H+H_2$ exchange reaction (Section IV, Publications, No. 2), using the realistic potential hypersurface of Porter and Karplus.[2] The results confirm the earlier coplanar studies and indicate that the formula of surprisal theory, appropriate to a single dynamical constraint condition (specifying the partitioning of energy between translational and internal rotational motion) holds accurately throughout the coordinate region of strong atom-molecule interaction, not just in the asymptotic region.

These quantum dynamical results indicate that the empirical success of surprisal analysis follows from pure quantum collision dynamics, without invoking separate statistical phenomena. At present, a valid derivation of surprisal theory from first principles appears to be lacking. Applications of surprisal theory were surveyed in a review article (Section IV,

Publications, No. 12), which discusses quantum dynamical studies analyzed by use of surprisal theory and examines implications for statistical theories of collision processes.

B. Fourier Transform Method for Molecular Collisions

Recent developments in the mathematical theory of classical dynamics have revitalized the long-dormant theory of semiclassical quantization. Practical semiclassical computational methods have been developed for bound states of systems with several nonseparable degrees of freedom. In particular, vibrational levels of triatomic molecules have been computed.

As discussed by Percival,[3] quantization conditions can be applied to an extended classical trajectory characterized by definite action integrals. The locus of a trajectory in phase space (coordinates and momenta as independent variables) is an invariant toroid, whenever action integrals, constant on such a toroid, are well-defined. Corresponding to action integrals as generalized momenta, the conjugate generalized coordinates are angle variables. The original coordinates and momenta used to construct the system Hamiltonian function can be represented as periodic functions of the angle variables for the trajectory corresponding to a given toroid. Percival considers constructing an invariant toroid directly as a geometrical object in phase space, by solving the nonlinear partial differential equations appropriate to this representation in action-angle variables. These equations can be solved iteratively in a Fourier transform representation. By constructing an invariant toroid, action integrals are computed as functions of energy. Semiclassical energy levels of a bound system correspond to quantized values of these action integrals.

Extension of this methodology to atom-molecule scattering problems might open up new prospects for semiclassical or approximate quantum dynamical calculations, especially for reactive collisions. As originally formulated, the theory cannot be applied to collision

problems. For unbounded motion, at least one of the frequency constants of the theory vanishes, and Percival's equations cannot be solved. However, by reflecting the scattering potential at an external boundary, inelastic scattering problems can be adapted to this methodology, and results for an inelastic scattering model were obtained (Section IV, Publications, No. 1). This construction cannot be used for reactive problems, because more than one reflection surface is required and the resulting potential function in general is not single-valued. In another application, the bound state formalism of Percival was used to parametrize vibrational potential functions for triatomic molecules (Section IV, Publications, No. 4).

An alternative method, suitable in principle for reactive collisions, was formulated and applied to model problems (Section IV, Publications, Nos. 7,8). An infinite potential barrier is introduced either to close off entry channels in the asymptotic region or to separate distinct potential wells. Toroids obtained for each of the resulting single-well regions are combined to describe motion in the original potential. The required boundary constraint, equivalent to specular reflection at the infinite barrier, is nonholonomic, expressed as inequalities to be satisfied by coordinate values. By augmenting the Fourier expansion with functions having discontinuous derivatives, the linearized equations to be solved at each step of iteration were expressed as a standard linear programming problem. The dual simplex method[4] of linear programming theory was adapted for solving them (Section IV, Publications, No. 20).

An internal potential barrier is a common feature of reactive collisions. It is not immediately obvious how to extend the concept of an invariant toroid to such a system. A similar problem occurs for bound motion in a double potential well. For energies below the internal barrier, two independent toroids are required, but they must coalesce for energies

above the barrier. Understanding the bound multiple-well problem is a prerequisite for understanding the reactive collision problem. The technique of imposing confinement within arbitrary boundaries makes it possible to consider such problems. The method was tested for a double well potential constructed from two Morse functions. The dynamical problem was solved as a single well with an infinite potential barrier at the internal potential maximum. Converged results were obtained both above and below the potential barrier. In another application, solutions were obtained separately for two unsymmetrical potential functions defined by setting an infinite potential barrier at the minimum of a Morse potential. These partial solutions were combined to produce accurate solutions of the Morse oscillator problem. The boundary constraint method was also used to obtain scattering solutions for a model problem with a positive Gaussian potential barrier. This made it possible to study the qualitative behavior of an invariant toroid near an energy of stagnation, defined by total energy equal to internal barrier height. The computational method was successful in approaching this limit from both higher and lower energies (Section IV, Publications, No. 21). In this work, a true second-order iterative method was introduced. All terms of first order in the residual nonlinearity were included in the linear equations solved exactly at each iteration. This made it possible to solve Percival's equations for bounded model problems with highly anharmonic potential functions.

A technical problem which has not yet been adequately solved for systems with more than one degree of freedom is that the matching surface between arrangement channels or distinct potential wells is not, in general, geometrically simple in both the natural coordinates and the true angle variable coordinates of the Fourier transform method. Moreover, the relationship between these two representations is not defined until a solution of the dynamical equations has been obtained. Calculations on $He+H_2$ indicate that choosing a

linear or planar surface, in the space of angle variables, to represent the matching surface is not a useful approximation. For further progress with this method, a self-consistent definition of the matching surface must be incorporated into the iterative computation.

C. Theoretical Methods for Electron Scattering

1. Multichannel variational methods. Electron scattering by atoms and molecules is characterized by complex short-range interactions and by long-range potential functions of simple known form. In order to exploit the simplicity of the long-range potentials, it is useful to consider *hybrid* theoretical methods in which variational treatment of the short-range problem is combined with exact numerical solution of the long-range problem. Exploratory studies of alternative methods have led to the adoption of a particular method for electron-molecule scattering calculations which combines the most favorable aspects of several earlier methods. Preliminary results obtained with this method are described in Section III-A, below. Results of the exploratory studies are summarized here.

Two principal methods have been used for accurate electron-atom scattering calculations: The R-matrix method[5] and the matrix variational method,[6] based on the Hulthén-Kohn variational principle. Methods based on the Lippmann-Schwinger integral equation,[7] or more specifically on the Schwinger variational principle[8] have more recently been shown to be viable. All of these methods can be applied to electron-molecule scattering. The standard close-coupling method is less suitable for molecules because it requires solution of coupled partial differential equations or, alternatively, strong mixing of spherical harmonics in a one-center expansion.

The R-matrix method exploits the applicability of different computational techniques for large and small radial coordinate r by explicitly introducing a boundary radius r_1. Basis

functions of the inner region are truncated at r_1 and asymptotic close-coupling equations are solved outside r_1. This method has been used successfully for electron-molecule scattering calculations.[9]

In the matrix variational method a basis set of localized (quadratically integrable) functions is augmented by auxiliary functions (continuum basis) that are oscillatory in the asymptotic region. Spherical Bessel functions have been used in calculations of electron scattering from neutral atoms.[6]

In a hybrid version of this method, continuum basis functions (numerical asymptotic functions, or NAFs) are obtained by explicit integration of the asymptotic close-coupling equations.[10] The NAF method has been used for accurate calculations of electron-atom and electron-ion cross sections.[11] Assuming exact solution of the asymptotic equations, only the residual Hamiltonian, a short-range operator, contributes to the integrals used in the Hulthén-Kohn variational formulas. Similar integrals, defined within a fixed spherical or spheroidal boundary, must be evaluated in the R-matrix method.

The common feature of hybrid methods, as this term is used here, is to use exact solutions of a model problem to simplify solution of the full physical scattering problem. The physical Hamiltonian operator is separated into a model part and a residual part. If model solutions are incorporated into a Green's function, the Schrödinger equation can be converted to a Lippmann-Schwinger integral equation, which must be solved for the effects of the residual Hamiltonian. As usually formulated, the Schwinger variational principle is derived from a Lippmann-Schwinger equation constructed from the free-particle Green's function. Hence, the long-range multipole potentials typical of electron scattering by atoms or molecules are retained in the residual Hamiltonian. An alternative formalism, which

reduces the residual Hamiltonian to a true short-range operator, has been derived[6] by

constructing the Green's function appropriate to exact solution of a multichannel model

problem, which could include all long-range multipole potentials (Section IV, Publications,

No. 9). This formalism should be competitive in efficiency to other hybrid methods

considered here. It has not yet been tested in calculations on atoms or molecules because it

cannot make use of existing bound-state computational methods and programs as readily as

do methods based on matrix representations of the Schrödinger equation.

In the matrix variational method,[6] matrix equations for the full $N+1$ electron problem,

one electron scattered by an N-electron target atom or molecule, are replaced by an

equivalent formal structure: a matrix optical potential that acts on an orthogonalized

continuum wave function. A model study (Section IV, Publications, No. 19) showed that

introducing a Bloch operator, at finite r_1, into the reduced one-electron continuum equations,

valid R-matrix results can be obtained even though all the integrals used in defining the

matrix optical potential are carried out to $r = \infty$. This method becomes equivalent to the

R-matrix method, except for the specific variational principle used and for the range of

integration, if the continuum basis can represent an exact solution of the asymptotic

differential equations outside r_1.

Because the phase of an asymptotic solution of the scattering problem must be

determined by solving the variational equations, two oscillatory basis functions differing in

asymptotic phase must be included in the continuum basis set for each open channel. If this

is done in variational R-matrix calculations, an exact asymptotic solution can be brought into

some radius $r=r_0$, much smaller than the usual boundary at r_1. The boundary radius r_1 must

be sufficiently large to justify neglecting nonlocal potentials. The remaining

energy-independent basis functions have only to represent the effects of deviations from the asymptotic Hamiltonian in the intermediate range $r_0 < r < r_1$.

This remark suggests that convergence of variational R-matrix calculations[6] can be facilitated by including two energy-dependent NAF basis functions for each open scattering channel. As originally formulated,[5] the R-matrix method for atoms and molecules uses basis functions with a fixed boundary condition at r_1. The resulting discontinuous slope at r_1 is corrected by introducing an energy-dependent basis function inside r_1.[12] In a model study (Section IV, Publications, No. 18), it was shown that calculations using either the matrix variational method or the R-matrix method with one energy-dependent oscillatory basis function per channel showed much better convergence, with respect to the number of bound basis functions used, than did the unmodified R-matrix method. The best convergence was found for the R-matrix method with two energy-dependent oscillatory functions per channel. This method is being implemented for electron-molecule scattering calculations, as reported in Section III-A, below.

2. *Theory of resonance and threshold effects.* The theory of dynamical coupling between electron scattering and nuclear motion in molecules is discussed in Section II-E, below. In computing rovibrational transition effects from electron-molecule scattering matrices obtained for fixed nuclei, the latter matrices must be analyzed in order to separate background scattering from specific resonance effects. The formal theory of multichannel resonances is well-known and can be used in this analysis. The corresponding theory of threshold structures had not previously been developed in a form that allows the separation of background scattering from the effects of singularities due to a Feshbach resonance, associated with an excitation threshold, or due to a virtual state. It was found possible to develop multichannel threshold theory in analogy to the theory of multichannel resonances,

making an explicit separation of background scattering from the effects of pole singularities (Section IV, Publications, Nos. 10 and 11).

3. *Algebraic and numerical methods.* A new iterative method for computing several eigenvalues and the corresponding eigenvectors of large matrices has been proposed (Section IV, Pulications, No. 15). The essential idea is to adapt the Jacobi algorithm to a partitioned matrix, so that only the first n columns are transformed if n eigenvalues are required. Test calculations indicate that for the lowest eigenvalue of a large matrix, this method converges in time comparable to the successive relaxation method. It converges equally efficiently for any specified number of eigenvalues, the computation time being proportional to this number.

Methods for iterative solution of large systems of linear equations have also been explored. Many variants of existing algorithms were tested on model problems. No single algorithm was found to be both reliable (ensuring convergence) and rapidly convergent for these test problems. However, a combination of two algorithms, both differing in detail from prior methods, was found to be satisfactory. Details are given elsewhere (Technical Proposal, this contract, April 1982).

In approximate treatments of electron impact excitation of molecular vibration or dissociation, analytic models of resonance theory require knowledge of the fixed-nuclei electronic resonance width as a function of electronic energy and of nuclear conformation. A new numerical technique has been devised for calculations based on earlier work by Hazi,[13] who used Stieltjes moment theory in the Feshbach resonance formalism. The new method is a practical procedure for converting a discrete representation of a Green's function, with a dense distribution of pole singularities, into a smooth approximation to the continuum limit of

such a function (Section IV, Publications, No. 16). The new method uses a finite-element representation of the pole strength function, or resonance width as a function of real energy for a scattering problem. The method has been successfully tested in applications to a model electron scattering problem, using the Feshbach resonance theory for a resonance phase shift. In a second application, the Schwinger variational formula was used to compute the total phase shift for the same model problem. The new numerical method was used to evaluate the Green's function integral required in the Schwinger formalism. From these two calculations, both resonance and background phase shifts are deduced, requiring only data computed from a discrete spectral representation of the model Hamiltonian.

The proposed method represents the pole strength distribution function by a linear spline function. This function is constructed from triangular finite elements. Correct threshold behavior is built in by using momentum or wave number k as independent variables, and by starting the first element at the continuum threshold. Since each triangular element has a finite and continuous Hilbert transform, a smooth fit is obtained to both real and imaginary parts of the limiting complex-valued function, corresponding, respectively, to the energy shift and width functions in the Feshbach resonance theory.

D. Electron Scattering by Atoms

Theoretical studies of low energy electron-atom scattering were supported by the predecessor of this contract. Methodology developed in this project was applied to quantitative calculations of electron scattering by He, Li, Na, K, C, N, and O atoms. Theory and computed results, and their experimental implications, were reviewed in a general survey of progress in this field (Section IV, Publications, No. 22). More details are given in a recently published book.[6]

Because the electron-helium elastic scattering cross section can be used as a standard for experimental calibration, accurate theoretical calculations are desirable. Variational calculations of s- and p-wave phase shifts for energies up to 19 eV were carried out, in calculations designed to give 1% accuracy for the differential elastic cross section (Section IV, Publications, Nos. 3 and 5). Agreement with high-precision experimental data from several laboratories is compatible with this level of accuracy, estimated from convergence studies of the variational calculations. The computed differential cross section is in current use as an experimental standard.

In the n=2 excitation region, e^-+He scattering exhibits several structural features associated with resonances, threshold effects, and with a virtual state.[6] These energy-dependent features of the cross section can be understood in terms of the eigenphase sums for the three lowest symmetry states ^{2}S, ^{2}P^0, and ^{2}D. Earlier variational calculations[14] were repeated with larger basis sets in an improved variational formalism (Section IV, Publications, No. 24). The recomputed eigenphase sums agree in their principal qualitative features with the earlier calculations, and are compatible with analytic structure expected from multichannel threshold analysis (Section IV, Publications, No. 10). The ^{2}S eigenphase sum shows structure associated with the well-known resonance at 19.37 eV and with a virtual state at the 2^1S threshold. There is a single broad ^{2}P^o resonance, below the 2^1S threshold, and a strong ^{2}P^o cusp at the 2^3P^o threshold. A broad ^{2}D resonance occurs below the 2^3P^o threshold. Cusp or rounded step features occur at all thresholds in channels with outgoing orbital s-waves.

E. Nuclear Motion in Electron-Molecule Scattering

A fundamental difficulty in the quantitative theory of electron-molecule scattering is the large number of internal states of the target system. Full close-coupling calculations in

the basis of rovibrational states are not, in general, feasible, because of the large number of coupled scattering channels. The EMA approximation[15] (Section IV, Publications, No. 6) is intended to provide a practical solution to this problem, exploiting analytic scattering theory and the Born-Oppenheimer approximation to extract detailed rovibrational excitation cross sections from fixed-nuclei electron scattering calculations.

The energy-modified adiabatic approximation (EMA) can be described in terms of the nuclear kinetic energy operator T_n in the full molecular Hamiltonian. Fixed-nuclei electron scattering calculations correspond to neglecting T_n, as in the Born-Oppenheimer limit of large nuclear mass. This reduces the nuclear Hamiltonian H_n to the potential energy V_n, a function of the internuclear coordinates. For a diatomic target molecule, the electronic wave function for fixed nuclei would be computed for a range of values of two parameters: internuclear distance R and electronic energy ε. When the electronic Schrödinger equation solved for fixed nuclei is compared with the rovibrational close-coupling equations, it is found that these systems of equations become formally identical if the parameter ε is replaced by the corresponding operator $E-H_n$. The electronic wave function, parametrically dependent on ε and R, becomes an operator (dependent on T_n) acting on rovibrational wave functions.

Electron scattering is determined from the asymptotic form, for large electronic radius r, of the electronic wave function. For fixed nuclei, this is specified by the scattering matrix $S(\varepsilon,R)$. The essential point of the EMA approximation is to replace $S(\varepsilon,R)$ by an operator $S(E-H_n,R)$, using forms of operator functions that are consistent with analytic scattering theory. The rovibrational scattering matrix is obtained by evaluating matrix elements of this operator in the basis of rovibrational wave functions.

When matrix elements of T_n can be neglected, the EMA approximation reduces to the well-established adiabatic-nuclei approximation.[16] This is true generally for pure rotational excitation,[17] but not in the vicinity of excitation thresholds and not for long-lived electronic resonance states. The EMA approximation gives vibrational excitation structure for $e^- + N_2$ in substantial agreement with experiment.[15] The adiabatic-nuclei approximation is not valid in this case because of the dominant effect of an electronic resonance.

An important goal of electron-molecule scattering theory is to develop quantitative methods for processes such as dissociation or chemical change induced by electron impact. A typical process, dissociative attachment, is

$$e^- + AB \rightarrow A + B^- \tag{1}$$

The standard theory[18] attributes this process to an electronic resonance state AB^- with a finite lifetime over some range of internuclear distance R, due to autodetachment. The AB^- potential curve is assumed to be a complex-valued function

$$W(R) = V(R) - \frac{i}{2} \Gamma(R) . \tag{2}$$

A wave packet (in coordinate R) initiated in the Franck-Condon region by electron capture loses amplitude as it moves outward. The survival probability in the limit of dissociation is a measure of the rate of dissociative attachment.

This theory runs into difficulties when there is relatively strong autodetachment, as discussed in a review article (Section IV, Publications, No. 17). The postulated complex-valued function may not be well-defined, or it may be multivalued. Scattering amplitudes computed by Klonover and Kaldor[19] for $e^- + H_2$, which give good agreement with experimental vibrational excitation cross sections, computed in the adiabatic-nuclei

approximation, were analyzed for the resonance functions $V(R)$ and $\Gamma(R)$ (Section IV, Publications, No. 23). The usual resonance formalism was found to be inadequate. The scattering amplitudes imply a strong energy-dependent nonresonant background.

A viable theory of dissociative attachment should be valid in the strong-coupling limit. Such a theory, based on the EMA approximation, has been proposed (Section IV, Publications, No. 13). This theory will be used for calculations on $e^- + H_2$, using scattering matrices obtained from new variational calculations, described below (Section III-A).

III. RESEARCH ACCOMPLISHED, FINAL CONTRACT PERIOD

A. Variational Calculation of $e^- + H_2$ Scattering

Model studies show that variational R-matrix theory and hybrid versions of the Kohn variational method can be organized so that principal computational steps are common to both methods. In order to take advantage of these theoretical developments, a collaboration has been initiated that includes P. G. Burke and C. J. Noble, at the Daresbury Laboratory, England; L. A. Morgan, at Royal Holloway College, England; and the present project. The general plan is to explore and design computational methods for electron-molecule scattering that can be built onto the existing ALCHEMY system[20] of bound state molecular wave function programs. The programs are at present limited to diatomic target molecules, using atomic basis orbitals of exponential form (STOs), augmented by continuum basis functions in the form of spherical Bessel functions and by numerical asymptotic functions (NAFs). Integrals required for calculations on polyatomic target molecules are currently being programmed. This work is described in Section III-E, below.

Methods and programs are being tested in calculations of $e^- + H_2$ scattering (Section IV, Publications, No. 30). Variational R-matrix calculations were carried out within the boundary radius $r_1 = 10.0a_0$, then matched to external solutions of the asymptotic coupled differential equations. The target H_2 ground state, $^1\Sigma_g^+$, is represented by the SCF wave function of Fraga and Ransil,[21] with a total of six σ atomic basis orbitals. An additional six π STOs were added in calculations taking $\sigma \to \pi$ polarizability into account.

In the static exchange approximation, only the target ground state is considered, represented by its static quadrupole potential in the asymptotic region. Converged results were obtained for coupled s and d partial waves in the $^2\Sigma_g^+$ scattering state, using only eight continuum basis functions in the form of NAFs and Bessel functions for k^2 up to $0.36a_0^{-2}$

(Section IV, Publications, No. 26). Earlier calculations, using only STOs on the scattering center with no true continuum basis, had required 13 such basis functions for convergence. Results for K-matrix elements, computed for the $^2\Sigma_g^+$ scattering state, are listed in Table 1. Earlier results of Collins *et al.*[22] are given for comparison. Compared with typical accurate bound state calculations, the orbital basis set used here is small, giving only 15 configuration state functions for the variational R-matrix basis. all calculations here are for internuclear separation $1.402a_0$.

Experience with electron-atom scattering calculations indicates that the polarization response of the target system to an incoming electron can be taken into account by including polarization pseudostates in the close-coupling formalism.[6] The SCF ground state wave function of H_2 is the single configuration $(1\sigma_g^2)\ ^1\Sigma_g^+$. Using methods described below, in Section III-D, pseudostate orbitals $\bar{\pi}_u$ and $\bar{\sigma}_u$ were computed variationally and were used to construct two pseudostate wave functions

$$(1\sigma_g\bar{\pi}_u)^1\Pi_u\ ,\ \ (1\sigma_g\bar{\sigma}_u)^1\Sigma_u^+\ . \tag{3}$$

For calculations involving the $^1\Pi_u$ pseudostate or manifold of virtual excitations, six basis STOs of π symmetry were added to the Fraga-Ransil σ orbital basis. The computed parallel and transverse polarizabilities are respectively

$$\alpha_\parallel = 7.0149a_0^3\ ,\ \ \alpha_\perp = 4.9660a_0^3\ , \tag{4}$$

to be compared with accurate values (at $R=1.40a_0$),[23]

$$\alpha_\parallel = 6.3805a_0^3\ ,\ \ \alpha_\perp = 4.5777a_0^3\ . \tag{5}$$

In order to include all components of the dipole transition moment from the $^1\Sigma_g^+$ ground state, the following scattering channels must be represented, if p and f partial waves are included in the ground state channels:

Target State	Partial Wave Orbital	
$^1\Sigma_g^+$	$p\sigma_u$ $f\sigma_u$	
$^1\Pi_u$	$d\pi_g$ $g\pi_g$	
$^1\Sigma_u^+$	$s\sigma_g$ $d\sigma_g$ $g\sigma_g$	(6)

Thus, a 2-channel static exchange calculation must be extended to seven channels for a consistent and comparable polarized pseudostate calculation. Calculations of this kind were carried out at $R = 1.402a_0$. Results for open-channel K-matrix elements are summarized in Table 2, and are compared with earlier calculations by Klonover and Kaldor,[19] who represented dynamical polarization effects by a second-order optical potential. In the present calculations, all components of dipole transition moments and of quadrupole moments were computed for the three target states. This matrix of moments was used to construct the asymptotic potential functions for integration of coupled equations outside the R-matrix boundary.

The continuum orbital basis in these calculations was carried to effective completeness by successively adding Bessel functions in each of the partial wave channels.

Alternative ways of including numerical asymptotic functions in the orbital basis set were tested. While two independent NAFs per open channel must be used to represent oscillatory functions over an extended range of the radial variable, the values of k and ℓ in the present calculations are such that the open-channel solutions of the asymptotic equations have few if any oscillations inside r_1, the R-matrix boundary. In order to avoid linear

dependency problems one regular vector NAF per open channel is constructed as a linear combination of the numerically integrated asymptotic functions by an algorithm described in Section III-C, below. The diagonal component of this function is fitted to a regular spherical Bessel function at a matching radius r_0, $2.0a_0$ in the present case, and is used as a continuum basis function. Completeness of the continuum basis inside r_1 is achieved by adding Bessel functions that vanish at r_1, with successively greater numbers of radial modes. Bessel functions were added in each of the seven partial wave channels until effective convergence to two or three significant decimals was achieved in the eigenphase sum. Convergence was smooth and rapid, requiring only 42 configuration state functions for the results listed in Table 2. Wave functions of the same structure were used over the full energy range studied.

The computed eigenphase sums shown in Table 2 are in good agreement with the earlier work of Klonover and Kaldor,[19] although the individual K-matrix elements differ more evidently. The systematic sign reversal of element K_{31} appears to be an artifact of a phase convention. The present calculations confirm the general trend of the Klonover-Kaldor eigenphase sums. This strengthens the argument,[24] sketched in Section II-E, above, that the e^-+H_2 scattering resonance is accompanied by a strongly energy-dependent background, not considered in the current theory of dissociative attachment.

These results represent the achievement of a major goal of this project. These are the first electron-molecule scattering calculations to include a full dynamical pseudostate model of molecular polarization. Special methods were developed to solve many technical problems associated with the asymptotic integration and construction of useable basis NAFs. Some of these developments are discussed in Section III-C, below.

B. Dynamical Distorted Wave Calculations

In order to compute accurate differential scattering cross sections, the partial wave representation must be summed to convergence. Long-range potentials lead to significant contributions from high-order partial waves. Accurate variational calculations are feasible only for a few low-order partial waves. Using the partial wave Born approximation,[6] partial wave phase shifts or K-matrix elements at any given energy can be estimated accurately for sufficiently large angular momentum ℓ. Following Thompson,[25] the Born scattering amplitude can be corrected for short-range effects by adding a sum of low-order partial wave corrections. The correction for each partial wave is computed by subtracting the partial wave Born scattering amplitude from that computed variationally. This method has been used for rare gas atoms to compute effects of the polarization potential $-\alpha/2r^4$ on the scattering amplitude.

A similar approach can be used for molecules. The asymptotic potential, through quadrupole terms for a diatomic molecule, is

$$V(r) = -(\alpha_0 + \alpha_2 P_2(\cos\theta))/2r^4 - QP_2(\cos\theta)/r^3 . \qquad (7)$$

Nonspherical terms here couple partial waves ℓ, $\ell \neq 2$, but the fixed-nuclei scattering amplitude and partial wave K-matrix can still be evaluated analytically for $\ell > 0$ in the first Born approximation. Molecular rotation must be taken into account as discussed in Section II-E, above.

Because of the difficulty of accurate variational calculations, it is desirable to limit such calculations to the smallest possible number of partial waves. For this reason, in the present work, a dynamical distorted wave approximation has been introduced. This is implemented by carrying full solutions of the asymptotic differential equations into the matching radius r_0,

then matching at r_0 onto a diagonal R-matrix appropriate to regular free-wave functions in all channels. This same construction, discussed in Section III-C, below, is used to define open-channel NAFs, used as basis functions in the full variational calculations. Hence, the dynamical distorted wave approximation should approach accurate variational results in the limit of negligible short-range interactions. This approximation should become accurate as ℓ increases for fixed k. Ultimately, it must also approach the Born limit, for large k, or, given k, for large ℓ. The general approach to be followed is to use the first Born approximation where valid, as in Thompson's method, correcting low-order partial wave scattering amplitudes by use of the dynamical distorted wave approximation in its range of validity, in turn corrected by accurate variational calculations for the lowest partial wave ℓ-values.

The dynamical distorted-wave approximation should be valid for partial waves with negligible amplitude inside the matching radius r_0, which is chosen as an approximate outer radius for the charge density of the target molecule. For example, $r_0 = 2.0a_0$ is used here for H_2. Given k and ℓ, classical trajectories pass outside the impact parameter or classical turning-point radius

$$r_{c\ell} = \left(\ell + \frac{1}{2} \right) \Big/ k , \qquad (8)$$

unless deflected strongly by the long-range scattering potential. This implies, unless the phase shift or diagonal K-matrix element is very large, that the quantum mechanical wave function is small inside this radius. Hence, a condition for validity of the dynamical distorted wave approximation is

$$r_{c\ell} >> r_0 . \qquad (9)$$

In the present calculations on H_2, for k-values up to $1.0a_0^{-1}$, this condition is

$$\ell \gg 1.5 . \tag{10}$$

Table 3 shows K-matrix elements from dynamical distorted wave calculations of $e^- + H_2$ scattering, at $R = 1.402a_0$, compared with converged variational calculations and with K-matrix elements deduced from scattering amplitudes of Klonover and Kaldor.[19] From Eq. (10), the distorted wave approximation should be valid for $\ell > 3$, marginally valid for $\ell = 3$, but should fail for $\ell = 1$. Comparing columns (a) and (b) in Table 3, matrix elements K_{11} are not a useful approximation to the variational values, but the elements K_{33} are accurate within 10-25%, in qualitative agreement with the argument leading to Eq. (10). The relative error is largest for the K elements of largest magnitude, as expected. It can be anticipated that elements with $\ell > 3$ are sufficiently accurate for use in Thompson's formula, but this has not yet been checked by variational calculations.

For scattering by an isotropic polarization potential, polarizability α in atomic units, the partial-wave Born approximation formula for the diagonal K-matrix element in a channel with partial wave orbital angular momentum ℓ is

$$K_{\ell\ell} = \frac{\pi\alpha k^2}{(2\ell + 3)(2\ell + 1)(2\ell - 1)} . \tag{11}$$

This formula is not exact in the present case, since it does not take into account the anisotropic polarization and static quadrupole potentials, Eq. (7). However, matrix elements K_{55} and K_{77} in Table 3, column (a), agree in magnitude with this formula. In contrast, the corresponding matrix elements from Klonover and Kaldor are smaller by several orders of magnitude. Without closer examination of the original calculations,[19] no explanation can be

suggested, but the long-range potentials do not appear to be correctly represented for higher partial wave components of the scattering amplitude in these earlier calculations.

C. Improved Computational Methods for Coupled-Channel Calculations

Outside the target molecule, electron scattering is described by coupled ordinary differential equations of the general form

$$(H^{(o)} - E)_{pp} u_{ps}(r) = - \Sigma_q V_{pq}(r) u_{qs}(r) , \quad p = 1, \cdots, n \tag{12}$$

where $V_{pq}(r)$ is a real symmetric matrix of asymptotic multipole potential functions. Efficient and accurate solution of these equations is important in the present project. They are used in at least three different contexts: first, inward integration from large r to the R-matrix boundary at r_1, to match external partial waves with specified asymptotic forms to a variational R-matrix; second, inward integration from r_1 to an inner matching radius r_0, to define numerical basis functions (NAFs) for the variational calculation; third, direct inward integration from large r to r_0 in the dynamical distorted wave approximation. Here r_1 is a radius beyond which nonlocal potentials can be neglected, and r_0 is a much smaller radius, beyond which the target multipole potentials are defined as inverse powers of r.

Integrations are done using a combination of methods. The Gailitis expansion[16] is used in the far asymptotic region, into a Gailitis radius r_G. Inside r_G, integrations are done with the R-matrix propagator method,[17] using a program described elsewhere.[28] The published methods are modified in several ways, to be described here.

A particular problem, in the present work, is the presence of strongly closed channels, due to the dynamical representation of the polarization response of a target molecule. Because all channels are dynamically coupled, noise terms which build up exponentially in either direction of propagation of closed-channel wave functions can spread to the open

channels, leading to severe loss of accuracy if functions are propagated over large coordinate ranges. The detailed methods used here are designed to eliminate this problem as much as possible.

In the far asymptotic region, solutions of Eq. (12) can be developed analytically. The Ansatz used by Gailitis,[26] following Burke and Schey,[29] is

$$u_{ps}(r) = \gamma_{ps}(r)w_s(r), \tag{13}$$

where all functions are complex, and $w_s(r)$ is a solution of the uncoupled equations for some channel s. Since $w_s(r)$ is the same for all channel components u_{ps}, and the multipole potential functions are constants times inverse powers of r, the coefficient functions $\gamma_{ps}(r)$ can be developed iteratively as series in inverse powers of r. In general, these are divergent (asymptotic) series, and the Gailitis radius r_G must be chosen sufficiently large to give adequate accuracy when such a series is truncated at its term of least magnitude.

In the present project (C. J. Noble and R. K. Nesbet, manuscript in preparation) the Gailitis power series is replaced by a continued fraction or Padé approximant. The effect is to bring r_G down to much smaller values in difficult cases, and also to take advantage of higher terms in the Gailitis series, beyond the truncation term of the asymptotic series. A general algorithm for replacing a given power series by a continued fraction (or diagonal Padé approximant) has been devised for this application (CFRACT algorithm: R. K. Nesbet, unpublished).

In order to describe the specialized integration methods used in the present project, several definitions are needed. Equations (12), which are second-order ordinary differential equations, have 2n independent vectorial local solutions at any given r where the potential functions are not singular. It is convenient to use two indices to denote a particular vector

solution (replacing the single index s). Then for $p=1,...,n$; $i=0,1$; $a=1,...,n$, the function $u_{pia}(r)$ denotes the component in channel p of solution i,a. Depending on context, index i denotes one of two independent solutions associated with channel a by specified boundary conditions. The multichannel Wronskian matrix is an invariant of integration. By a suitable choice of boundary conditions, the Wronskian can be put into a canonical form,

$$W_{ia,jb} = \sum_p (u'_{pia} u_{pjb} - u_{pia} u'_{pjb})$$

$$= (\delta_{i0}\delta_{j1} - \delta_{i1}\delta_{j0})\delta_{ab} . \tag{14}$$

This is an elementary antisymmetric matrix

$$J = \begin{bmatrix} O & I \\ -I & O \end{bmatrix} . \tag{15}$$

If Eq. (12) are integrated between r_1 and r_2, values and derivatives of any vectorial solution at the two boundaries are related by 2n linear equations:

$$\underset{\sim}{u}(1) = - R_{11}(1,2)\underset{\sim}{u}'(1) + R_{12}(1,2)\underset{\sim}{u}'(2) ,$$

$$\underset{\sim}{u}(2) = - R_{21}(1,2)\underset{\sim}{u}'(1) + R_{22}(1,2)\underset{\sim}{u}'(2) . \tag{16}$$

The array of coefficients here,

$$\begin{bmatrix} R_{11}(1,2) & R_{12}(1,2) \\ R_{21}(1,2) & R_{22}(1,2) \end{bmatrix} , \tag{17}$$

defines the *global* R-matrix, which is a real symmetric $2n \times 2n$ matrix. The conventional definition of the R-matrix, denoted here as a *local* R-matrix, refers to a particular subset of n solutions of Eq. (12) such that at r_1 and r_2,

$$\underset{\sim}{u}(1) = r_1 R(r_1) \underset{\sim}{u}'(1) \ ,$$

$$\underset{\sim}{u}(2) = r_2 R(r_2) \underset{\sim}{u}'(2) \ . \tag{18}$$

The local R-matrix is a real symmetric $n \times n$ matrix. Given $R(r_1)$ and the global R-matrix, propagation equations for $R(r_2)$ are obtained by substituting Eqs. (18) into Eqs. (16). In the R-matrix propagator method,[17] this transformation is carried out for successive sectors of a subdivided interval (r_1, r_2). In the method used here,[28] global R-matrices are computed variationally for each sector.

Regular boundary conditions at the origin of coordinates $(r=0)$ define a subset of n solutions of Eq. (12). In conventional R-matrix calculations, a local R-matrix is computed variationally at r_1, then propagated out to r_G where it is matched to asymptotic solutions to obtain the scattering matrix or K-matrix. In the present work, adapting this method to inward integration, the sectorial global R-matrices are combined in each propagation step to form a global R-matrix defined between current extreme boundaries, eventually building up the global R-matrix : r the full interval (r_1, r_G). This matrix is stored for subsequent use. Inward integration is continued, building up a global R-matrix for the interior interval (r_0, r_1), which is used to construct NAFs. These functions are used in the variational calculation of the local matrix $R(r_1)$, which is propagated out to r_G, using the previously stored global R-matrix for the interval (r_1, r_G). Matching to Gailitis solutions at r_G completes the calculation.

It is convenient to define *canonical solutions* of Eq. (12) as those with canonical Wronskian, $W = J$, and to define linear transformations that preserve the Wronskian, as *canonical transformations*.[6] If $u'_{pia}(r)$ and $u_{pia}(r)$ are combined to define a column vector

(n components of $\underset{\sim}{u}'$ followed by n components of $\underset{\sim}{u}$) the array of vectors $\underset{\sim}{u}_{ia}$ defines a 2n×2n square matrix U. In this notation, Eq. (14) takes the simple form,

$$U^\dagger J U = J \tag{19}$$

where notation (†) denotes the transpose of a real matrix. If solution vectors obtained by a linear transformation are denoted by

$$V = UQ , \tag{20}$$

then it follows from Eq. (19) that the defining condition for a canonical transformation is

$$Q^\dagger J Q = J . \tag{21}$$

Canonical transformations form a group. In particular, local values of vector solutions as represented by the array U belong to this group.

The Gailitis functions are defined to have canonical Wronskian W=J by requiring $w_s(r)$ in Eqs. (13) to be Coulomb-Bessel functions with standard normalization, or appropriate decreasing exponential functions for closed channels. An accurate Wronskian at finite r is a necessary condition for the validity of the Gailitis expansion. When used as a test, this shows, in general, a very great improvement at given r when the inverse power series of the Gailitis expansion is replaced by a continued fraction representation. To reduce subsequent errors, an algorithm has been devised which cleans up a given approximate solution matrix U by enforcing certain internal symmetries that are a property of canonical transformation matrices (FCANON algorithm: Section IV, Publications, No. 28). FCANON is routinely applied to functions evaluated from the Gailitis expansion in the present work.

If wave functions are propagated through classically forbidden regions, small errors are amplified by exponential factors. This can cause severe computational problems when closed

channels are present in Eq. (12). This loss of accuracy is a property of the system of coupled differential equations, not of any particular method of integrating these equations. These exponential factors do not occur if R-matrices are propagated rather than wave functions. Hence, propagation of functions should be avoided in favor of R-matrix propagation whenever possible, as is done in the procedures described above.

It is not possible to avoid function propagation in constructing NAFs, which are used as variational basis functions. In the present work, the global R-matrix for interval (r_0, r_1) is built up from sectors without referring to the propagated functions, which are constructed at sector boundaries from the global R-matrix and from initial values at r_1. Within each sector, each NAF is represented by an expansion in Legendre polynomials.

Coupling to strongly closed channels causes large errors to accumulate when functions are propagated over the external range (r_1, r_G). From Eqs. (16), the crucial equation for inward integration over an interval (r_1, r_2) is

$$R_{21} \underset{\sim}{u}'(1) = R_{22} \underset{\sim}{u}'(2) - \underset{\sim}{u}(2) \tag{22}$$

which must be solved for $\underset{\sim}{u}'(1)$. Then $\underset{\sim}{u}(1)$ is obtained directly from Eqs. (16). It is convenient to symmetrize the operator acting on $\underset{\sim}{u}'(1)$ in Eq. (22), which becomes

$$R_{12} R_{21} \underset{\sim}{u}'(1) = R_{12}(R_{22} \underset{\sim}{u}'(2) - \underset{\sim}{u}(2)) , \tag{23}$$

then to diagonalize the resulting matrix

$$R_{12} R_{21} = \Sigma_\mu \lambda_\mu \underset{\sim}{e}_\mu \underset{\sim}{e}_\mu^\dagger \tag{24}$$

and to construct $\underset{\sim}{u}'(1)$ for the solution vector indexed by (ia) in the form

$$\underset{\sim}{u}'_{ia}(1) = \Sigma_\mu \underset{\sim}{e}_\mu \lambda_\mu^{-1} d_{\mu, ia} , \tag{25}$$

where

$$d_{\mu,ia} = \underset{\sim}{e}_\mu \cdot R_{12}(R_{22}\underset{\sim}{u}'_{ia}(2) - \underset{\sim}{u}_{ia}(2)) . \tag{26}$$

In considering examples of closed-channel system, it is found that, in general, a number of eigenvalues λ_μ equal to the number of closed channels n_{cl} become very small if integration is carried out over an extended range. The coefficients $d_{\mu,ia}$ also become small, but not enough to remove the exaggerated effect of roundoff errors amplified by the factors λ_μ^{-1} in Eq. (25). Using $e^- + H_2$ scattering as a model problem, with polarization pseudostate channels included, detailed calculations show that the λ_μ^{-1} factors can amplify roundoff errors at r_G enough to destroy the accuracy of functions at r_1 (Section IV, Publications, No. 28). The proposed solution to this problem is to carry out a linear transformation of the given functions at r_G so that the coefficients $d_{\mu,ia}$ of Eq. (26) are reduced to zero while retaining the decoupling of unbounded closed-channel functions from all other functions, as required by physical boundary conditions. In the PROJ algorithm (Section IV, Publications, No. 28), this is done by subtracting multiples of the bounded closed-channel function vectors from the open-channel vectors at r_G. Since there are n_{cl} small eigenvalues λ_μ, this gives n_{cl} equations for n_{cl} unknowns, for both values of index i in Eqs. (26). The actual transformation of functions leads to very small changes at r_G, since the correction terms are decreasing exponential functions of r, but the induced effect at r_1 is large. This transformation can be justified by this observation: an adjustment at the noise level of physical boundary conditions at r_G is used to eliminate terms which are clearly identified as amplified noise at r_1. Since the PROJ linear transformation is not canonical, it is followed by the FCANON algorithm to produce functions at r_1 with a correct Wronskian. These functions are propagated inwards to r_0, as described above, with no further auxiliary

transformations. Numerical tests show that the accuracy of functions propagated over a large interval is improved if the PROJ and FCANON algorithms are used as described here.

Partial wave solutions of a scattering problem must be regular at $r=0$ and bounded at large r. For n channels, n_{op} open and n_{cl} closed, at arbitrary given energy or k-value, there are only n_{op} regular, bounded solutions. These solutions can be constructed as linear combinations of $2n-n_{cl}$ bounded functions obtained by inward integration, starting at large r with functions that vanish in all but one asymptotic channel. The n_{cl} unbounded asymptotic functions are to be excluded. In standard scattering theory, external solutions would be matched at some matching radius r_0 to an internal R-matrix. A similar construction, expressed in the form of a canonical transformation of the integrated solutions, is used in the present work to define NAFs, giving one regular bounded variational basis function for each open channel. Use of the remaining irregular functions will be discussed below.

Since the asymptotic potentials are not accurate inside some radius r_0, NAFs can be matched at r_0 to arbitrary regular functions. For convenience, a diagonal R-matrix is constructed from the known logarithmic derivatives of Coulomb-Bessel functions for open channels, or powers of r for closed channels. This diagonal R-matrix is matched to n_{op} external functions of the form

$$f_{p0s} = u_{p0s} + \Sigma_q u_{p1q} K_{qs} ,\qquad (27)$$

where $p,q=1,...,n$; $s=1,...,n_{op}$, by solving for the K-matrix:

$$\Sigma_q (u_{p1q}(r_0) - r_0 R_{pp} u'_{p1q}(r_0)) K_{qs}$$

$$= - (u_{p0s}(r_0) - r_0 R_{pp} u'_{p0s}(r_0)) . \tag{28}$$

The Wronskian condition ensures that the open-channel submatrix K_{pq} is symmetric, but the elements K_{ps} for closed channels s are not determined. A full $n \times n$ symmetric matrix can be defined by assigning values

$$K_{ps} = K_{sp} , \quad p \text{ open} ,$$

$$K_{ps} = 0 , \quad p \text{ closed} , \tag{29}$$

It can easily be verified that if K is a full $n \times n$ symmetric matrix, as in Eq. (29), that the $2n \times 2n$ matrix

$$Q = \begin{bmatrix} I & O \\ K & I \end{bmatrix} \tag{30}$$

satisfies the defining conditions for a canonical transformation, Eq. (21). This canonical transformation of the integrated solutions is used to define regular NAFs for use as variational basis functions.

When irregular NAFs are needed to represent a phase-shifted continuum function, they must be matched at some point to functions that are regular at small r. Consideration of typical functional forms indicates that this secondary matching point should be at approximately the first zero of the corresponding regular function. In exploratory calculations on $e^- + H_2$ it was found for the range of energies and partial wave ℓ-values considered (Section III-A, above) that this secondary matching point was well outside r_0, and for a large part of the energy range, even outside r_1. Because of this, to avoid

redundancy in the variational basis set, only regular NAFs were used for each partial wave, and Bessel functions were added for completeness.

D. Molecular Moments and Polarizabilities

The ALCHEMY program system is designed for efficient calculations of individual molecular electronic bound states. Reorganization of these programs was required in order to compute transition multipole moments between different states, in general of different total symmetry. This reorganization was carried out as part of the present project (C. J. Noble and R. K. Nesbet, unpublished). The resulting program package computes target state wave functions, energies, static moments, and transition moments in a single computer job.

Construction of polarization pseudostates is an option of the revised program package. Polarizability is defined as an energy correction of second order in external electric field intensity, computed from the first-order perturbed wave function. Pseudostate orbital functions can be deduced from the density matrix connecting the unperturbed and first-order perturbed wave functions. At present, construction of pseudostate orbitals has been implemented only for single-configuration unperturbed wave functions.

E. Integrals for Polyatomic Molecular Scattering

Because multicenter Coulomb integrals can be evaluated in closed form, calculations of bound-state electronic wave functions for polyatomic molecules are greatly facilitated by use of Gaussian basis orbital functions. Since R-matrix calculations require integration over a finite volume, this simplifying property of Gaussian orbitals is not directly useful in such calculations. Polyatomic electron scattering calculations require new methods for simplifying the multicenter integrals.

In the present project, the approach being followed is based on a translation theorem for Gaussian functions.[30,31] This provides an analytic representation in the spherical polar coordinates about a specified center of a solid harmonic Gaussian defined about another center. The radial functions about the specified center can be evaluated as finite sums. For certain ranges of the angular parameters, these sums are affected by severe numerical cancellation. An alternative representation, a symmetric infinite series in both radial coordinates has been derived and studied (R. Seeger, unpublished notes). It is found that this series can be summed readily by converting to a continued fraction or Padé approximant, using the CFRACT algorithm (Section III-C, above). The radial functions can be evaluated efficiently for arbitrary parameter values by use of one or the other of these two representations.

Programs have been written and tested for all one-electron integrals involving a mixed basis of Gaussian orbitals and continuum Bessel functions or NAFs. Kinetic energy integrals are evaluated in a symmetric form appropriate to a generalization of variational R-matrix theory to enclosed volumes of arbitrary shape, discussed in Section III-F, below. Work on two-electron integrals is in progress (Section IV, Publications, No. 31).

F. Extensions of R-Matrix Theory

In considering variational R-matrix calculations for polyatomic molecules, it is interesting to examine the possible adaptation of the theory to volumes enclosed by surface of irregular shape. Ultimately, such a development, valid for a Wigner-Seitz polyhedron or for an irregular cluster composed of an adsorbed molecule and several near-neighbor substrate atoms, would open up new areas of quantitative theory in solid-state or surface physics. The conceptual essence of the R-matrix theory is that the Schrödinger equation is solved in a strictly delimited closed volume, to obtain complete information required for

matching wave functions on the surface of that volume. Techniques for eliminating a common interface between two adjacent R-matrix cells can be extended indefinitely, so that the global R-matrix for a larger cell of complex structure can be built up from modular units corresponding to subcells. A new variational principle, suitable for such applications, will be described here.

The R-matrix theory is formulated for a multichannel one-electron Schrödinger equation. An N+1-electron problem can be reduced to this form by projecting onto N-electron core or target states. The derivation here will be presented for the simplified case of a single core state, or equivalently, for an effective one-electron Schrödinger equation

$$(h - \varepsilon)\psi = 0 \tag{31}$$

The generalization to multiple core states is immediate.

Consider solution of Eq. (31) in a volume Ω of arbitrary shape, enclosed by a boundary surface Σ. In spherical polar coordinates, for a spherical surface, the global R-matrix is indexed by spherical harmonic functions on this surface. Here, this definition is generalized to a linear integral R-operator whose kernel is defined in arbitrary coordinates by

$$\psi(1) = \int R(1,2) \nabla_n \psi(2) d\Sigma_2 \tag{32}$$

for points (1,2) on surface Σ. It is convenient to define a reciprocal operator, the generalized logarithmic derivative $\Lambda(1,2)$, such that

$$\nabla_n \psi(1) = \int \Lambda(1,2) \psi(2) d\Sigma_2 , \tag{33}$$

for the normal gradient at point 1 on surface Σ.

A variational principle for the logarithmic derivative of a radial wave function was derived by Kohn.[32] [See References 6, p. 51]. The proposed variational principle for the linear operator Λ follows essentially the same logic. The variational functional is

$$\Xi = \int_\Omega \psi^*(h - \epsilon)\psi d\tau , \tag{34}$$

which vanishes if Eq. (31) is solved throughout the closed region Ω. Integrating the kinetic energy matrix element by parts, this becomes

$$\Xi_\Lambda = \int_\Omega \left(\frac{1}{2} \nabla\psi^* \cdot \nabla\psi + \psi^*(V - \epsilon)\psi \right) d\tau$$

$$- \frac{1}{2} \int \int_\Sigma \psi^*(1) \Lambda(1,2) \psi(2) d\Sigma_2 d\Sigma_1 . \tag{35}$$

Treating Λ as fixed, for an infinitesimal variation $\delta\psi$, the variation of Ξ_Λ is

$$\delta\Xi_\Lambda = \int_\Omega \delta\psi^*(h - \epsilon)\psi d\tau + \frac{1}{2} \int_\Sigma \delta\psi^* (\nabla_n \psi - \int_\Sigma \Lambda\psi d\Sigma_2) d\Sigma_1$$

$$+ \text{complex conjugate} . \tag{36}$$

This vanishes for unconstrained variations of ψ if and only if Eq. (31) is satisfied throughout the interior of Ω and if Eq. (33) holds on the boundary surface Σ.

If ψ is expanded as a linear combination of linearly independent basis functions ϕ_a, so that

$$\psi = \sum_{a=1}^{n} \phi_a c_a , \tag{37}$$

then

$$\Xi_\Lambda = \Sigma_a \Sigma_b c_a^* (A_{ab} - B_{ab}) c_b , \tag{38}$$

where

$$A_{ab} = \int_\Omega \left(\frac{1}{2} \nabla\phi_a^* \cdot \nabla\phi_b + \phi_a^*(V - \epsilon)\phi_b \right) d\tau \tag{39}$$

and

$$B_{ab} = \frac{1}{2} \int_\Sigma \int_\Sigma \phi_a^*(1) \Lambda(1,2) \phi_b(2) d\Sigma_2 d\Sigma_1 . \tag{40}$$

Variation of Ξ_Λ with respect to the coefficients c_a gives the system of linear equations

$$\Sigma_b A_{ab} c_b = \Sigma_b B_{ab} c_b , \tag{41}$$

$$= \frac{1}{2} \int_\Sigma \int_\Sigma \phi_a^*(2) \Lambda(2,3) \psi(3) d\Sigma_3 d\Sigma_2 . \tag{42}$$

Solving Eqs. (42) for the coefficients c_a, Eq. (37) becomes

$$\psi(1) = \frac{1}{2} \Sigma_b \phi_b(1)(A^{-1})_{ba} \int_\Sigma \int_\Sigma \phi_a^*(2) \Lambda(2,3) \psi(3) d\Sigma_3 d\Sigma_2 . \tag{43}$$

Consistency of these equations requires the kernel of the R operator, the reciprocal of Λ, to be

$$R(1,2) = \Lambda^{-1}(1,2) = \frac{1}{2} \Sigma_b \phi_b(1)(A^{-1})_{ba} \phi_a^*(2) , \tag{44}$$

defined for points (1,2) on surface Σ. It should be noted that the matrix A_{ab} is Hermitian in general, or real symmetric if the basis function ϕ_a are real. It follows that the Λ and R operators are Hermitian, or symmetric if real-valued.

To use Eq. (44), a discrete representation of functions on surface Σ can be introduced. In general, different representations can be used on different portions of the closed surface, as might be convenient, for example, for different faces of a polyhedron. The R operators for nonoverlapping but adjacent cells can be concatenated by solving algebraic equations

indexed by the basis functions for a common representation on the surface of intersection.

If Eq. (44) is specialized to spherical geometry, it reduces to a variant of the usual formula for the R-matrix. Conventional treatment of the radial Schrödinger equation uses r-multiplied radial functions rather than just the radial factors of three-dimensional functions. This shifts an integrated radial term between Eqs. (39) and (40), altering both equations in a consistent manner. The resulting R-matrix differs from the generalized R operator of Eq. (32) for the same reason.

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This geometrically covariant formalism was developed in the present project originally to check kinetic energy integrals and surface terms for internal consistency. It is presently being incorporated into new programs for electron scattering by polyatomic target molecules. Possible applications in solid-state or surface physics are being investigated.

G. Optical Potential and Shadow Scattering

When many coupled channels must be considered, solution of the matrix Schrödinger equations can be simplified if the coupled equations are replaced by an optical potential in each channel, such that

$$(H^{(o)} - E)_{pp} u_{ps}(r) = -V^{opt}_{ps} u_{ps}(r) , \qquad (45)$$

which replaces Eq. (12). In general, a true optical potential is nonlocal and energy dependent. The Ansatz given by Eq. (13), due to Burke and Schey[29] and used by Gailitis,[26] was originally introduced to provide an analytic development of asymptotic solutions of Eq. (12). Analysis of Eqs. (12) and (45) in terms of this Ansatz shows that it provides an analytic development not only of asymptotic wave functions but also of the optical potential (Section IV, Publications, No. 27).

Substitution of Eq. (13) into Eqs. (12) and (45) gives

$$V_{ps}^{opt} \gamma_{ps} w_s = \Sigma_q V_{pq} \gamma_{qs} w_s . \qquad (46)$$

If w_s is a complex-valued oscillatory solution of the uncoupled equations, Wronskian conditions prevent both real and imaginary parts from vanishing simultaneously. Hence, this function can be factored out of Eq. (46) to give

$$V_{ps}^{opt}(r) = \Sigma_q V_{pq}(r) \gamma_{qs}(r) \gamma_{ps}^{-1}(r) . \qquad (47)$$

This is an optical potential expressed as a complex function of r, given wave vector k and angular momentum ℓ appropriate to channel p. For consistency, index s must be equated to p by fixing the asymptotic phase and normalization of functions $u_{ps}(r)$ in a diagonal-channel representation.

This construction of V^{opt} can be carried out as an expansion in powers of r^{-1} for large r or as a power series in $r-r_a$ about some r_a. As an example of the method, a coupled pseudostate model of scattering by a polarizable isotropic target gives

$$V^{opt}(r) = \frac{1}{2} \alpha(- r^{-4} + (2ik/\Delta E)r^{-5} + O(r^{-6})) \qquad (48)$$

where α is the polarizability and ΔE is the pseudostate excitation energy. Equation (48) adds an energy-dependent absorptive term to the well-known dipole polarization potential. The derivation assumes that all channels are open, requiring $E > \Delta E$.

This optical potential formalism has been developed to simplify calculations of high-order partial wave terms in electron-molecule scattering. Equation (47) makes it possible to consider shorter-range corrections to Eq. (7), in which the polarization potential is the limiting asymptotic form of the optical potential due to closed pseudostate channels.

Equation (48) has an immediate application in interpreting recent experimental data on extreme forward scattering of 15-25 keV electrons by rare gas atoms (Section IV, Publications, No. 29). A strong forward peak and rapid angular variation, essentially a Fraunhofer diffraction pattern, were observed,[33] and were interpreted as a diffraction pattern due to shadow scattering. The removal of forward electron flux due to inelastic scattering, which dominates elastic scattering by a factor $k^2 a_0^2$ in the forward direction, is expected to affect the elastic cross section analogously to the scattering effect of a black disc, whose shadow is described by a Fraunhofer pattern.

Despite this simple physical picture, no published theoretical work leads to such a diffraction pattern for electron-atom scattering. The first Born elastic cross section is nearly independent of angle in the range of interest (below 10 mrad). To simplify the theory, so that exact results could be obtained for a realistic model, a pseudostate model was used, giving exact target atom polarizability. The second Born scattering amplitude was computed for $e^- + H$ atom scattering, using the exact $\ell = 1$ pseudostate.[34] The second Born elastic cross section was found to have no strong forward peak and no oscillations at small angles. The imaginary part of the forward scattering amplitude agrees in second order with the optical theorem, in which it is determined by the large total inelastic cross section.

These results can be reconciled by considering the two leading terms of the complex optical potential, given by Eq. (48). The WKB phase shifts due to this potential are complex. For the ground state of atomic hydrogen α is $4.5a_0^3$ and ΔE is $(18/43)\, e^2 a_0^{-1}$. Assuming a core radius of $1.0a_0$, the imaginary term in the optical potential introduces a damping factor $\exp(-5.375)$ into all partial wave scattering matrix elements with $\ell + 1/2$ less than kr_0. The resulting effective shadow in the forward direction is expected to produce a

diffraction pattern similar to that derived for a complex square well model potential.[35] This has not yet been verified by detailed calculations.

Both terms in Eq. (48) are quadratic in the transition amplitude, compatible with the second Born approximation. However, the damping effect is so large in the shadow region that a low-order Born approximation, essentially a power series expansion of an exponential function with large negative argument, cannot be valid. Hence, specific effects of shadow scattering, such as the forward diffraction pattern, cannot usefully be treated by a low-order Born approximation.

H. Spin-Selective Electron Scattering by Magnetic Material

Spin-dependent elastic scattering of polarized electrons by an amorphous ferromagnetic material has recently been observed.[36] Spin asymmetry was measured in elastic backscattering from $Ni_{40}Fe_{40}B_{20}$, in its ferromagnetic state, and from a similar pure Fe glass. The spin asymmetry is defined by

$$S = (i_+ - i_-)/(i_+ + i_-) , \qquad (49)$$

where i_+ and i_- are, respectively, the intensities of elastically backscattered electrons with spin parallel and antiparallel to the majority spin of the target. To avoid pure spin-orbit scattering, incident electron spin is oriented to lie in the scattering plane. In the experiment on a pure Fe glass, the spin asymmetry was found to vary with incident energy almost identically with the NiFe data. Thus, the observed strong energy dependence and sign reversals must be attributed to Fe. As in scattering by liquid metals, the observed intensity is proportional to $\sigma\lambda$, where σ is an atomic elastic cross section and λ is the mean free path, determined by inelastic scattering.

In a recent review article, Pierce and Celotta[37] concluded that these data have no satisfactory theoretical explanation. The fact that S changes sign as a function of energy conflicts with energy dependence expected from current theory. Using ideas from the theory of the electron-atom scattering, it has been shown (Section IV, Publications, No. 25) that the energy dependence of the observed spin asymmetry is compatible with the onset of a 3p→3d excitation process, at 50 eV, and with a scattering resonance of the nature of an inverse Auger process just below this excitation threshold. These inelastic and resonant elastic scattering processes are spin-selective because of the ferromagnetic polarization of 3d states.

The proposed explanation of these data differs significantly from current spin-polarized LEED theory,[38] especially in considering spin-selective scattering effects of localized excitations. By implication, an unpolarized electron beam incident on a magnetic target must produce partially polarized scattered electrons. In this mode, these scattering effects are spin-productive.

The observed asymmetry S changes sign from negative to positive near 50 eV (vacuum energy). This can be accounted for by an inverse Auger resonance below the 3p→3d localized excitation threshold. If the initial state of Fe is approximately $3p^6 3d^6 4s^2$, an electron with sufficient energy can be captured temporarily into a resonance state of Fe⁻ with configuration $3p^5 3d^8 4s^2$. In a metal, the local charge imbalance would be compensated by conduction electron relaxation. This resonance state could exist only if two localized hole states are available. In Fe, this would be true only for minority spin electrons. The resonance energy can be estimated from the MVV Auger line in Fe, centered at 43 eV above the Fermi level.[39] If the work function is 4.5 eV, elastic scattering of minority spin

electrons should show resonance structure centered at 38.5 eV, contributing to the observed negative spin asymmetry structure below 50 eV.

The postulated MVV resonance is associated with a 3p→3d localized excitation. This transition is observed[40] at 54.4 eV in Fe, relative to the Fermi level. When corrected for the work function, this places an inelastic threshold at 49.9 eV. Inelastic exchange scattering due to the excitation process is spin-selective to the extent that predominantly minority-spin hole states are available for the final 3d state. Inelastic scattering of minority-spin electrons decreases their mean free path λ and hence decreases their backscattered elastic intensity, which is proportional to λ. The net effect is a positive contribution to the spin asymmetry S, commencing at the inelastic threshold energy.

For Fe, an inverse Auger elastic scattering resonance below the 3p→3d threshold, accompanied by stronger inelastic scattering starting at that threshold, could cause the spin asymmetry for elastic backscattering to be negative at 38.5 eV and to change sign near 50.0 eV, in agreement with the observed data.

A localized 3p→3d^2 resonance should not exist fo Ni, since two localized 3d hole states would not be compatible with the known atomic moment and band structure. However, enhanced inelastic scattering of minority-spin electrons should occur above the 3p→3d excitation threshold. The optical transition[40] is at 66.2 eV relative to the Fermi level, or 61.7 eV for electrons in vacuo. Comparison of the NiFe data[36] with data for a pure Fe glass shows a positive enhancement of the spin asymmetry above 60 eV due to Ni, but no significant effect at lower energies. This behavior agrees qualitatively with the present argument.

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V. PERSONNEL AND FACILIFIES[*]

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Education

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1954-1957	Lincoln Laboratory, MIT, Research Associate.
1958-1959	RIAS, Martin Company, Baltimore, Staff Member (summers).
1969-1961	NIH Special Research Fellow, Institut Pasteur, Paris.
1956-1962	Boston University, Assistant, Professor of Physics (appointed Associate Professor in 1962).
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Participation

IBM participation in contract: 50% (cost-sharing).

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[*]All facilities are IBM owned.

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TABLE 1

$e^- + H_2$ Static Exchange, K-Matrix Elements in the $^2\Sigma_g^+$ Scattering State

$k(a_0^{-1})$	K_{00} a	b	K_{20} a	b	K_{22} a	b
0.1	−0.2172	−0.217	0.3589(−2)	0.39(−2)	0.2248(−2)	0.21(−2)
0.2	−0.4504	−0.451	0.7107(−2)	0.73(−2)	0.4346(−2)	0.45(−2)
0.3	−0.7227	−0.722	0.1038(−1)	0.11(−1)	0.7237(−2)	0.74(−2)
0.4	−1.0661	−1.07	0.1316(−1)	0.13(−1)	0.1107(−1)	0.11(−11)

a. Present results, $R = 1.402a_0$.

b. Collins *et al.*, Reference 22.

c. $0.n \times 10^{-m}$ is written as $0.n(-m)$.

TABLE 2

e⁻+H$_2$ Polarized Pseudostate, K-Matrix Elements and Eigenphase Sums in the $^2\Sigma_u^+$ Scattering State

$k(a_0^{-1})$	K$_{11}$ a	b	K$_{31}$ a	b	K$_{33}$ a	b	Σ_η a	b
0.1	0.2493–1		0.1123–2		0.1662–2		0.2659–1	
0.2	0.9422–1		0.2391–2		0.4415–2		0.9836–1	
0.3	0.2356	0.1827	0.3973–2	–0.1165–2	0.7688–2	0.1629–2	0.2391	0.18 23
0.4	0.4549	0.3885	0.6350–2	–0 7644–2	0.1111–1	0.6913–2	0.4380	0.37 74
0.5	0.7211	0.6225	0.9697–2	–0.2828–2	0.1632–1	0.1710–1	0.6410	0.57 39
0.6	0.9939	0.9455	0.1357–1	–0.1542–1	0.2451–1	0.3056–1	0.8068	0.78 78
0.7	0.1238+1	0.1220+1	0.1696–1	–0.3831–1	0.3261–1	0.4393–1	0.9236	0.9272
0.8	0.1400+1	0.1489+1	0.2263–1	–0.3023–1	0.3775–1	0.5358–1	0.9882	0.1033+1
0.9	0.1519+1	0.1673+1	0.2776–1	–0.1572–1	0.4304–1	0.6026–1	0.1031+ 1	0.1092+1
1.0	0.1591+1		0.3249–1		0.5196–1		0.1061+1	

[a]Present results, R=1.402a$_0$

[b]Data from Klonover and Kaldor, Reference 19, R=1.40a$_0$.

TABLE 3

e⁻+H$_2$ Polarized Pseudostate, K-Matrix Elements in the $^2\Sigma_u$ Scattering State, Dynamical Distorted Wave Approximation

$k(a_0^{-1})$	0.3				0.6			0.9	
	a	b	c	a	b	c	a	b	c
K_{11}	0.1034	0.2356	0.1827	0.2050	0.9939	0.9455	0.2124	0.1519+1	0.1673+1
K_{31}	0.3702-2	0.3973-2	-0.1165-1	0.7313-2	0.1357-1	-0.1542-1	0.8816-2	0.2776-1	-0.1572-1
K_{33}	0.8445-2	0.7688-2	0.1629-2	0.2641-1	0.2451-1	0.3056-1	0.5377-1	0.4304-1	0.6026-1
K_{51}	0.6729-6		0.9187-6	0.1031-4		0.7085-4	0.3644-4		0.2104-3
K_{53}	0.1014-2		-0.7265-6	0.2201-2		-0.4707-4	0.3455-2		-0.2701-3
K_{55}	0.2534-2		0.3349-9	0.7575-2		0.9912-7	0.1519-1		0.2836-5
K_{71}	0.6075-9		-0.3134-9	0.4142-8		-0.1133-6	-0.8338-8		-0.8129-6
K_{73}	0.2547-7		0.1432-9	0.5732-6		0.2722-7	0.3702-5		0.5614-6
K_{75}	0.4649-3		-0.6972-13	0.9930-3		-0.9817-10	0.1573-2		-0.1026-7
K_{77}	0.1160-2		0.1569-12	0.3313-2		0.1431-12	0.6476-2		0.4211-10

[a]Dynamical distorted wave approximation, present results, $R=1.402a_0$.

[b]Converged variational calculations, present results, $R=1.402a_0$.

[c]Data from Klonover and Kaldor, Reference 19, $R=1.40a_0$

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